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No single point $M_0$ need be preferred. If $\bar{u}(M)$ is summable with respect to $h(M_0,M)$ on the frontier of $T$ when $M_0$ is some definite point in $T$, it is summable on the frontier of $T$ with respect to $h(M_1,M)$, $M_1$ being any point of $T$.[14]

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[1] *Proc. Amer. Acad. Sci., Boston,* **41,** 1905–06.

[2] Borel, E., *Leçons sur les fonctions monogènes,* Paris, 1917, p. 10.

[3] Evans, *Rend. R. Accad. Lincei,* (Ser. 5), **28,** 1919 (262–265).

[4] For example it is sufficient to consider merely rectangles. See also the class Γ below.

[5] de la Vallée Poussin, C., *Integrales de Lebesgue,* Paris, 1916, p. 57.

[6] Volterra, V., *Leçons sur les fonctions de lignes,* Paris, 1913, chapt. II. It is to be noted that the definitions of continuity in the case of functions of curves and in the case of functions of point sets do not correspond at all to the same situation.

[7] The discontinuities need not be of the first kind.

[8] By $\{\psi(M)\}^2$ is meant the quantity $\{\psi_x(M)\}^2 + \{\psi_y(M)\}^2$.

[9] *Bull. Amer. Meth. Soc.,* **25,** November, 1918 (65–68).

[10] de la Vallée Poussin, C., *loc. cit.,* p. 98; *Trans. Amer. Math. Soc.,* **16,** 1915 (493).

[11] This identity is given for the special case of a rectangle, where the integrals (19) do not have to be used, by W. H. Young, *Proc. London Math. Soc.,* (Ser. 2), **16,** 1917.

[12] Osgood, *Lehrbuch der Funktionentheorie,* Leipzig, 1912, p. 151.

[13] Osgood and Taylor, *Transactions of the American Mathematical Society,* 14, 1913 (277–298).

[14] A complete exposition of the theorems of this paper will appear in an early issue of the *Rice Institute Pamphlet.*

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# *THERMO-ELECTRIC ACTION AND THERMAL CONDUCTION IN METALS: A SUMMARY*

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I shall now undertake to show in brief what I have accomplished in the series of papers which for some years I have been publishing in these PROCEEDINGS in relation to thermo-electric action and thermal conduction in metals.

Starting with the hypothesis of dual electric conduction, that is, conduction maintained in part by the passage of electrons from atomic union to atomic union during the contacts of atoms with positive ions, and in part by "free" electrons in the comparatively weak fields of force called the inter-atomic spaces, I derived[1] an equation giving the conditions of steady state in a detached bar hot at one end and cold at the other, and two equations for the conditions of equilibrium at a junction of two metals.

For the detached bar the steady state is a current of associated electrons up the temperature gradient and an equal current of free electrons down the temperature gradient. This involves a freeing of electrons from atomic unions, ionization, at the hot end of the bar, with absorption of heat, and re-association at the cold end, with evolution of heat. Evidently this is a process of conveying heat, and the question at once arises whether it is capable of accounting for the whole or any considerable part of thermal conduction in metals.

At the junction of two metals, on the other hand, the conditions of equilibrium permit no cyclic or circulatory motion of the electrons.

In a later paper[2] I introduced the following assumptions: That $n$, the number of free electrons per cu. cm. of the metal, is expressed by the equation

$$n = zT^q, \tag{1}$$

where $T$ is absolute temperature while $z$ and $q$ are constants. That $(k_f \div k)$, the ratio of free-electron conductivity to total conductivity, is given by the equation

$$(k_f \div k) = C + C_1 t + C_2 t^2, \tag{2}$$

where $t$ is temperature on the ordinary centigrade scale and $C$, $C_1$, $C_2$, are constants.

That the heat of ionization, in ergs, per electron is

$$\lambda' = \lambda_c' + 2.5RT, \tag{3}$$

where $\lambda_c'$ is a constant[3] and $R$ is the gas-constant for a single molecule.

In a still later paper[4] I rejected (3) and put in its place

$$\lambda' = \lambda_c' + sRT, \tag{3'}$$

where $s$ is a constant never less than 2.5. This change involved the revision of all the tables of numerical values contained in the paper in which equation (3) was used.

Equations (1), (2) and (3′) introduced for each metal seven characteristic constants, $z$, $q$, $C$, $C_1$, $C_2$, $\lambda_c'$ and $s$, but $z$ may for the most part be left out of consideration, as the definite numerical value of $n$ is needed only incidentally[5] in what follows.

To determine the six other constants for any metal we need six equations. Let us suppose that we know for each metal the value of the Thomson effect, $\sigma$, the value of the heat conductivity at 0° C., $\theta_0$, and at 100° C., $\theta_{100}$.

My expression for $\sigma$ is in the form

$$\sigma = K + (K_1 + K_2 t)T, \tag{4}$$

in which $K$, $K_1$ and $K_2$ are determined functions of $q$, $C$, $C_1$, etc. Bridgman's experiments give me the values of $K$, $K_1$ and $K_2$, for many metals, and so from the Thomson effect I get three equations, which are too long to be given here.

My expression for thermal conductivity is

$$\theta = \frac{R^2}{e^2}\left(\frac{\lambda_c'}{R} + sT\right)\frac{k_a k_f}{k}(s + q - 1.5), \tag{5}$$

in which $k_a$, the "associated-electron" conductivity, is $(k-k_f)$. With the known values of $\theta_0$ and $\theta_{100}$ I get two more equations involving the six characteristic quantities to be determined for each metal.

Thus for two metals, $\alpha$ and $\beta$, with twelve characteristic quantities to be determined, I have ten equations given by the properties of the metals, each metal being considered separately. When the two metals are brought into contact at 0° C. and again at 100° C., I have two Peltier-effect equations of the form

$$\Pi = \left(\frac{k_f}{k}\right)_\beta \lambda_\beta - \left(\frac{k_f}{k}\right)_\alpha \lambda_\alpha \qquad (6)$$

one for each temperature, where $\lambda_\beta$ is the heat, in ergs, required to free $(1 \div e)$ electrons within $\beta$, and $\lambda_\alpha$ has a like meaning for $\alpha$.

Thus I have twelve equations to determine the twelve constants in question.

If my theory were perfect and my experimental data complete, every constant could be found exactly, or to any desired degree of precision, by means of the equations here mentioned; but neither of these conditions is fulfilled. It is unlikely, for example, that equation (1) holds strictly through any considerable range of temperature. The experimental data I have used are doubtless incorrect to some extent, and in several places I have had to fill observational gaps by rather hazardous methods, particularly in values of thermal conductivity. Somewhat arbitrarily I have chosen to treat Bridgman's values of $\sigma$ as strictly correct, though he does not so regard them. I have done the same with regard to the available values of $k_o$, $k_{100}$, $\theta_o$, and $\Pi_o$. Accordingly the values of $\theta_{100}$ and $\Pi_{100}$ worked out from my equations are subject to the accumulated errors of theory and data, and it is not very disconcerting to find them differing considerably in some cases from the observed values or those indicated by other evidence.

If the question is raised why values of the constants cannot be found that will satisfy all of the equations, even if some of the data are inaccurate, the answer is that not all values are available for these constants, thus $C$, $q$, $\lambda_c'$, and $s$ must all be positive quantities.

Below are given for each of many metals, and for two alloys, the values of the six constants that I have hit on to account, as well as may be, for the observed or estimated values of the Thomson effect, thermal conductivity, and Peltier effect with respect to bismuth, in these substances. It is to be remembered that the algebraic sign which I give to the Thomson effect in any metal is opposite to the one ordinarily used; for example, I call $\sigma$ positive in iron and negative in copper. The Peltier effect, $\Pi$, is given as the amount of heat, in ergs, absorbed by $(1 \div e)$ electrons in going from the metal in question to bismuth. Thermal conductivities are given in calories/cm., sec., deg. C. The constant part, $\lambda_c'$, of $\lambda'$ is given in ergs; $\delta_c$ is the "ionizing potential," in volts, corresponding to $\lambda_c'$; $\delta_o$ and $\delta_{100}$, respectively, are the ionizing potentials, in volts, for the total work of ionization at 0° C. and at 100° C.; $k$ is electric conductivity in absolute measure. The numbers in the horizontal lines marked *Calc.*

are those which my formulae yield when the given values of the constants are put into them.

ALUMINIUM

| $C$ | $C_1 \times 10^6$ | $C_2 \times 10^8$ | $q$ | $s$ | $\lambda'_c \times 10^{16}$ | $\delta_c$ | $\delta_o$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| 0.0846 | −2.85 | 6.19 | 1.45 | 5.64 | 176 | 0.011 | 0.142 | 0.190 |
|  | $\sigma$ (in ergs/° C.) |  | $\theta_0$ | $\theta_{100}$ | $\Pi_o \times 10^{-4}$ | $\Pi_{100} \times 10^{-4}$ | $k \times 10^6$ | $k_{100} \times 10^6$ |
| Data | $(-0.016 + 0.006t)T$ |  | 0.477 | 0.492 | 202 | 263 | 380 | 265 |
| Calc. | $(-0.016 + 0.006t)T$ |  | 0.478 | 0.445 | 201 | 210 |  |  |

BISMUTH

| $C$ | $C_1 \times 10^6$ | $C_2 \times 10^8$ | $q$ | $s$ | $\lambda'_c \times 10^{16}$ | $\delta_c$ | $\delta_o$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| $0.19^0$ | −80.4 | 0 | 1.2 | 4.35 | 1088 | 0.068 | 0.169 | 0.206 |
|  | $\sigma$ (ergs/° C.) |  | $\theta_o$ | $\theta_{100}$ | $\Pi_o \times 10^{-4}$ | $\Pi_{100} \times 10^{-4}$ | $k_o \times 10^6$ | $k_{100} \times 10^6$ |
| Data | $-3.2T$ |  | 0.0202 | 0.0161 | 0 | 0 | 9.30 | 6.46 |
| Calc. | $-3.2T$ |  | 0.0201 | 0.0164 | 0 | 0 |  |  |

COBALT

| $C$ | $C_1 \times 10^6$ | $C_2$ | $q$ | $s$ | $\lambda'_c \times 10^{16}$ | $\delta_c$ | $\delta_o$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| 0.134 | 175 | 0 | 1.55 | 5.26 | 32 | 0.002 | 0.125 | 0.170 |
|  | $\sigma$ (ergs/° C.) |  | $\theta_o$ (6) | $\theta_{100}$ (6) | $\Pi_o \times 10^{-4}$ | $\Pi_{100} \times 10^{-4}$ | $k_o \times 10^6$ | $k_{100} \times 10^6$ |
| Data | $7.8T$ |  | 0.161(?) | 0.164(?) | 156 | 172 | 102 | 74.7 |
| Calc. | $7.8T$ |  | 0.160 | 0.177 | 154 | 117 |  |  |

COPPER

| $C$ | $C_1 \times 10^6$ | $C_2$ | $q$ | $s$ | $\lambda'_c \times 10^{16}$ | $\delta_c$ | $\delta_o$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| 0.068 | −16.6 | 0 | 1.49 | 6.8 | 64 | 0.004 | 0.162 | 0.221 |
|  | $\sigma$ (ergs/° C.) |  | $\theta_o$ | $\theta_{100}$ | $\Pi_o \times 10^{-4}$ | $\Pi_{100} \times 10^{-4}$ | $k_o \times 10^6$ | $k_{100} \times 10^6$ |
| Data | $-0.966T$ |  | 0.920 | 0.908 | 211 | 280 | 650 | 455 |
| Calc. | $0.966T$ |  | 0.928 | 0.866 | 211 | 229 |  |  |

GOLD

| $C$ | $C_1 \times 10^6$ | $C_2 \times 10^9$ | $q$ | $s$ | $\lambda'_c \times 10^{16}$ | $\delta_c$ | $\delta_o$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| 0.070 | −16.3 | 8.7 | 1.49 | 6.7 | 48 | 0.003 | 0.159 | 0.217 |
|  | $\sigma$ (ergs/° C ) |  | $\theta_o$ | $\theta_{100}$ | $\Pi_o \times 10^{-4}$ | $\Pi_{100} \times 10^{-4}$ | $k_o \times 10^6$ | $k_{100} \times 10^6$ |
| Data | $(-0.934 + 0.00t)T$ |  | 0.699 | 0.703 | 211 | 280 | 490 | 351 |
| Calc. | $(-0.934 + 0.00t)T$ |  | 0.696 | 0.666 | 210 | 227 |  |  |

### IRON

| $C$ | $C_1 \times 10^6$ | $C_2 \times 10^3$ | $q$ | $s$ | $\lambda' c \times 10^{16}$ | $\delta_C$ | $\delta_o$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| 0.02 | 12.1 | 19.9 | 1.2 | 15 | 128 | 0.008 | 0.348 | 0.487 |
|  | $\sigma$ (ergs/° C.) |  | $\theta_o$ | $\theta_{100}$ | $\Pi_o \times 10^{-4}$ | $\Pi_{100} \times 10^{-4}$ | $k_o \times 10^6$ | $k_{100} \times 10^6$ |
| Data | $(1.78 + 0.0516t)T$ |  | 0.163 | 0.151 | 247 | 310 | 78 | 48.1 |
| Calc. | $(1.78 + 0.0516t)T$ |  | 0.164 | 0.146 | 251 | 226 |  |  |

### MAGNESIUM

| $C$ | $C_1 \times 10^8$ | $C_2 \times 10^8$ | $q$ | $s$ | $\lambda' c \times 10^{16}$ | $\delta_C$ | $\delta_o$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| 0.061 | −13.8 | 0 | 1.499 | 6.8 | 608 | 0.038 | 0.196 | 0.255 |
|  | $\sigma$ (ergs/° C.) |  | $\theta_o$ | $\theta_{100}$ | $\Pi_o \times 10^{-4}$ | $\Pi_{100} \times 10^{-4}$ | $k_o \times 10^6$ | $k_{100} \times 10^6$ |
| Data | $-0.008T$ |  | 0.376(?) (7) | ? | 203 | 266 | 240 | ? |
| Calc. | $-0.008T$ |  | 0.374 |  | 202 | 220 |  |  |

### MOLYBDENUM

| $C$ | $C_1 \times 10^6$ | $C_2 \times 10^8$ | $q$ | $s$ | $\lambda' c \times 10^{16}$ | $\delta_C$ | $\delta_o$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| 0.053 | −64.4 | 10.8 | 1.3 | 8 | 176 | 0.011 | 0.197 | 0.266 |
|  | $\sigma$ (ergs/° C.) |  | $\theta_o$ | $\theta_{100}$ | $\Pi_o \times 10^{-4}$ | $\Pi_{100} \times 10^{-4}$ | $k_o \times 10^6$ | $k_{100} \times 10^6$ |
| Data | $(-4.33 + 0.015t)T$ |  | 0.43(8) | 0.42(8) | 219 | 319 | 274 | 191 |
| Calc. | $(-4.33 + 0.015t)T$ |  | 0.43 | 0.358 | 217 | 252 |  |  |

### NICKEL

| $C$ | $C_1 \times 10^6$ | $C_2$ | $q$ | $s$ | $\lambda' c \times 10^{16}$ | $\delta_C$ | $\delta_o$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| 0.132 | 84.9 | 0 | 1.6 | 5.0 | 176 | 0.011 | 0.127 | 0.170 |
|  | $\sigma$ (ergs/° C.) |  | $\theta_o$ | $\theta_{100}$ | $\Pi_o \times 10^{-4}$ | $\Pi_{100} \times 10^{-4}$ | $k_o \times 10^6$ | $k_{100} \times 10^6$ |
| Data | $0.0356T$ |  | 0.143 | 0.138 | 155 | 187 | 93 | 62.5 |
| Calc. | $0.0356T$ |  | 0.142 | 0.134 | 153 | 136 |  |  |

### PALLADIUM

| $C$ | $C_1 \times 10^6$ | $C_2$ | $q$ | $s$ | $\lambda' c \times 10^{16}$ | $\delta_C$ | $\delta_o$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| 0.083 | 64.3 | 0 | 1.6 | 6.51 | 139 | 0.0087 | 0.160 | 0.216 |
|  | $\sigma$ (ergs/° C.) |  | $\theta_o$ | $\theta_{100}$ | $\Pi_o \times 10^{-4}$ | $\Pi_{100} \times 10^{-4}$ | $k_o \times 10^6$ | $k_{100} \times 10^6$ |
| Data | $3.52T$ |  | 0.165 | 0.182 | 188 | 232 | 100 | 75.9 |
| Calc. | $3.52T$ |  | 0.165 | 0.179 | 188 | 182 |  |  |

### Platinum

| $C$ | $C_1\times10^6$ | $C_2$ | $q$ | $s$ | $\lambda'_c\times10^{16}$ | $\delta_C$ | $\delta_0$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| 0.0808 | 50.8 | 0 | 1.6 | 6.24 | 176 | 0.011 | 0.157 | 0.210 |
| | $\sigma$ (ergs/° C.) | | $\theta_0$ | $\theta_{100}$ | $\Pi_0\times10^{-4}$ | $\Pi_{100}\times10^{-4}$ | $k_0\times10^6$ | $k_{100}\times10^6$ |
| Data | $2.67T$ | | 0.164 | 0.173 | 195 | 245 | 110 | 79.3 |
| Calc. | $2.67T$ | | 0.167 | 0.170 | 194 | 195 | | |

### Silver

| $C$ | $C_1\times10^6$ | $C_2$ | $q$ | $s$ | $\lambda'_c\times10^{16}$ | $\delta_C$ | $\delta_0$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| 0.0663 | −14.2 | 0 | 1.49 | 7.1 | 64 | 0.004 | 0.169 | 0.230 |
| | $\sigma$ (ergs/° C.) | | $\theta_0$ | $\theta_{100}$ | $\Pi_0\times10^{-4}$ | $\Pi_{100}\times10^{-4}$ | $k_0\times10^6$ | $k_{100}\times10^6$ |
| Data | $-0.864T$ | | 1.009 | 0.992 | 210 | 279 | 670 | 476 |
| Calc. | $-0.864T$ | | 1.018 | 0.964 | 209 | 226 | | |

### Thallium

| $C$ | $C_1\times10^6$ | $C_2\times10^8$ | $q$ | $s$ | $\lambda'_c\times10^{16}$ | $\delta_C$ | $\delta_0$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| 0.0625 | 3.48 | 2.69 | 1.48 | 7.3 | 160 | 0.01 | 0.180 | 0.243 |
| | $\sigma$ (ergs/° C.) | | $\theta_0$ | $\theta_{100}$ | $\Pi_0\times10^{-4}$ | $\Pi_{100}\times10^{-4}$ | $k_0\times10^6$ | $k_{100}\times10^6$ |
| Data | $(0.268 + 0.0034t)T$ | | 0.090[8] | 0.096[8] | 208 | 271 | 57 | 43.9 |
| Calc. | $(0.268 + 0.0034t)T$ | | 0.090 | 0.094 | 209 | 221 | | |

### Tin

| $C$ | $C_1\times10^6$ | $C_2$ | $q$ | $s$ | $\lambda'_c\times10^{16}$ | $\delta_C$ | $\delta_0$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| 0.0654 | 2.36 | 0 | 1.51 | 6.66 | 368 | 0.023 | 0.179 | 0.236 |
| | $\sigma$ (ergs/° C.) | | $\theta_0$ | $\theta_{100}$ | $\Pi_0\times10^{-4}$ | $\Pi_{100}\times10^{-4}$ | $k_0\times10^6$ | $k_{100}\times10^6$ |
| Data | $0.134T$ | | 0.157 | 0.145 | 204 | 266 | 105 | 72.6 |
| Calc. | $0.134T$ | | 0.154 | 0.142 | 204 | 220 | | |

### Tungsten

| $C$ | $C_1\times10^6$ | $C_2$ | $q$ | $s$ | $\lambda'_c\times10^{16}$ | $\delta_C$ | $\delta_0$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| 0.042 | −35 | 0 | 1.48 | 11.4 | 40 | 0.0025 | 0.268 | 0.366 |
| | $\sigma$ (ergs/° C.) | | $\theta_0$ (9) | $\theta_{100}$ (9) | $\Pi_0\times10^{-4}$ | $\Pi_{100}\times10^{-4}$ | $k_0\times10^6$ | $k_{100}\times10^6$ |
| Data | $-341T$ | | ? | ? | 207 | 285 | 140 | 106 |
| Calc. | $-341T$ | | 0.352 | 0.335 | 208 | 234 | | |

ZINC

| $C$ | $C_1\times10^6$ | $C_2$ | $q$ | $s$ | $\lambda'_c\times10^{16}$ | $\delta_C$ | $\delta_o$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| 0.0613 | 16.7 | 0 | 1.55 | 7 | 240 | 0.015 | 0.178 | 0.238 |
|  | $\sigma$ (ergs/° C.) |  | $\theta_o$ | $\theta_{100}$ | $\Pi_o\times10^{-4}$ | $\Pi_o\times10^{-}$ | $k_o\times10^4$ | $k_{100}\times10^{16}$ |
| Data | $0.99T$ |  | 0.266 | 0.262 | 211 | 274 | 180 | 127 |
| Calc. | $0.99T$ |  | 0.266 | 0.258 | 212 | 225 |  |  |

CONSTANTAN

| $C$ | $C_1\times10^6$ | $C_2$ | $q$ | $s$ | $\lambda'_o\times10^{16}$ | $\delta_C$ | $\delta_o$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| 0.135 | 141 | 0 | 1.55 | 6.65 | 48 | 0.003 | 0.158 | 0.215 |
|  | $\sigma$ (ergs/° C.) |  | $\theta_o$ | $\theta_{100}$ | $\Pi_o\times10^{-4}$ | $\Pi_{100}\times10^{-4}$ | $k_o\times10^6$ | $k_{100}\times10^6$ |
| Data | $7.94T$ |  | 0.052 | 0.064 | 108 | 106 | 20.4 | 20.4 |
| Calc. | $7.94T$ |  | 0 052 | 0.076 | 108 | 55 |  |  |

MANGANIN

| $C$ | $C_1\times10^6$ | $C_2\times10^8$ | $q$ | $s$ | $\lambda'_o\times10^{16}$ | $\delta_C$ | $\delta_o$ | $\delta_{100}$ |
|---|---|---|---|---|---|---|---|---|
| 0.050 | −98 | 4.07 | 1.51 | 9.65 | 54 | 0.0034 | 0.228 | 0.311 |
|  | $\sigma$ (ergs/° C.) |  | $\theta_o$ | $\theta_{100}$ | $\Pi_o\times10^4$ | $\Pi_{100}\times10^4$ | $k_o\times10^6$ | $k_{100}\times10^6$ |
| Data | $(-0.828-0.0067t)T$ |  | 0.051 | 0.063 | 207 | 275 | 23.8 | 23.8 |
| Calc. | $(-0.828-0.0067t)T$ |  | 0.051 | 0.068 | 206 | 223 |  |  |

The preceding tabulation deals with every metal and alloy for which I have the necessary data, except cadmium, and for this metal, as I have shown elsewhere,[10] there is some reason for doubting the correctness of the data, Bridgman's value for $\sigma$ in cadmium being about ten times as large as that found by other investigators.

In the table that follows, $\gamma$ is the estimated ratio, expressed in per cents, of the number of free electrons to the number of atoms, including the positive ions, within the metal at 0° C. In arriving at the given value of $\gamma$ I have made use of the equation

$$k = \frac{nlce^2}{4RT} \qquad (7)$$

for the free-electron conductivity. The second member differs from Drude's familiar expression for the total conductivity, supposed by him due entirely to the free electrons, only in having 4 instead of 6 in the denominator. I have taken $l$, somewhat arbitrarily but not without regard to what others have done in this particular, as equal to ten times the centre to centre distance of adjacent atoms.

In columns II and III are given, in absolute units, the values of the potential gradient urging the associated electrons up the temperature gradient, at 0° C. and 100° C., respectively. $P$ is potential due to electric charge, and $(dP/dT)$ seems open to electrostatic measurement. $P_a$ is potential due to differential attraction of the unequally heated metal for the associated electrons, and $(dP_a/dT)$ does not seem within reach of direct experiment at present. Integrated from 0° C. to 100° C., $d(P + P_a)/dT$ gives differences of potential ranging from about 0.0026 volt in iron to about 0.0065 volt in bismuth and in cobalt and about 0.008 volt in constantan.

Column IV gives values of the "ionizing potential," in volts, within the metals at 0° C., and column V shows what these values would be at 2727° C., or 3000° absolute, if the equation

$$\lambda' = \gamma'_c + sRT$$

held all the way to that temperature.

Nothing exact can be expected from such an extrapolation, which takes no account of melting or of vaporization, but it is interesting to note that the values of $\delta$ thus obtained are of the same order of magnitude as those found by direct experiment on the vapors of metals, though still somewhat smaller than these latter values.

Column VI shows, in calories, the amount of heat absorbed by the free ions and by the process of ionization in heating 1 cu. cm. of the metal 1° C. in the neighborhood of 0° C. The former of these quantities is $1.5R\gamma n$, and the latter $dn/dT.\lambda' = qn\lambda'/T$, each reduced to calories. Column VII gives the thermal capacity, per cu. cm., of the metals as found by experiment.

| | I $\gamma$ % | II $\left[\frac{d(P+Pa)}{dT}\right]_0$ | III $\left[\frac{d(P+Pa)}{dT}\right]_{100}$ | IV $\delta$ at 0° C. | V $\delta$ at 2727° C. | VI | VII |
|---|---|---|---|---|---|---|---|
| Aluminium | 10.5 | −4070 | −4050 | 0.142 | 1.46 | 0.212 | 0.54 |
| Bismuth | 1.0 | −6620 | −6340 | 0.169 | 1.18 | 0.009 | 0.29 |
| Cobalt | 4.9 | −6120 | −6920 | 0.125 | 1.35 | 0.139 | 0.86 |
| Copper | 11.7 | −3970 | −3870 | 0.162 | 1.75 | 0.388 | 0.80 |
| Gold | 11.4 | −4030 | −3940 | 0.159 | 1.72 | 0.260 | 0.60 |
| Iron | 0.7 | −2530 | −2680 | 0.348 | 3.85 | 0.038 | 0.85 |
| Magnesium | 11.1 | −3550 | −3550 | 0.196 | 1.78 | 0.224 | 0.40 |
| Molybdenum | 4.4 | −3540 | −3110 | 0.197 | 2.06 | 0.099 | 0.70 |
| Nickel | 3.1 | −5790 | −6160 | 0.127 | 1.29 | 0.093 | 0.89 |
| Palladium | 2.6 | −4720 | −5080 | 0.160 | 1.68 | 0.069 | 0.57 |
| Platinum | 2.9 | −4410 | −4680 | 0.157 | 1.69 | 0.078 | 0.67 |
| Silver | 15.2 | −4050 | −3960 | 0.169 | 1.82 | 0.365 | 0.58 |
| Thallium | 1.8 | −3910 | −3960 | 0.180 | 1.88 | 0.027 | 0.36 |
| Tin | 3.2 | −3700 | −3720 | 0.179 | 1.73 | 0.052 | 0.39 |
| Tungsten | 1.9 | −4120 | −3770 | 0.268 | 2.92 | 0.072 | 0.64 |
| Zinc | 3.2 | −3720 | −3820 | 0.178 | 1.81 | 0.093 | 0.64 |
| Constantan | 0.7 | −7780 | −8590 | 0.158 | 1.71 | 0.024 | 0.85 |
| Manganin | 0.3 | −4180 | −4060 | 0.228 | 2.47 | 0.013 | 0.77 |

Evidently any number given in column VI should be smaller than the corresponding number given in column VII; and this is the case; but, for aluminium, copper, gold, and magnesium the ratio approaches one-half, and for silver it is greater than one-half. This is a larger value of the ratio than seems probable; that is, one might expect for these metals, if the values of column VI are true, greater departures from the law of Dulong and Petit than they really show. It is to be remembered, however, that the values of $\gamma$, upon which the numbers given in column VI depend, are based on the assumption that the mean free path of the free electrons within a metal is in all cases ten times the centre to centre distance of adjacent atoms. If we assume longer paths, we get correspondingly smaller values in columns I and VI. According to Compton and Ross[11] a photo-electrically excited electron can move in gold about twenty times the centre to centre distance of the atoms.

In view of the fact that the known specific heats of metals are in some cases smaller and in some cases larger than the law of Dulong and Petit requires, one may allow himself considerable latitude in dealing with the distribution of heat energy among the various degrees of freedom of the atoms. It is perhaps worth while to note that the numbers given in column VI would be larger if calculated for a temperature above 0° C., as this fact suggests at least an explanation of the general increase in the specific heats of metals with rise of temperature. More exact knowledge than we now have concerning the rate of this increase is greatly to be desired.

Doubtless my theory of heat conduction will be criticized as failing to deal in any general way with the Wiedemann-Franz law. This law is by no means exact. According to Jäger and Diesselhorst the ratio $(\theta \div k)$ varies, at 18°C., from $6.36 \times 10^{10}$ in aluminium to $9.64 \times 10^{10}$ in bismuth, while the temperature coefficient of this ratio varies from 0.15% in bismuth to 0.46% in platinum and palladium. In dealing theoretically with the relations of thermal to electrical conductivity we may proceed in either of two ways. We may seek for such a mechanism of conduction and such a general formula as will give the W.-F. law and then undertake to show why the individual metals depart from it, or we may proceed at first without any regard to this law but finally treat each metal in such a way as to explain its more or less approximate conformity with the law. The latter is the method I have followed.

I do not claim complete success in this undertaking. Some of the expedients I have adopted—for example, the values of $s$ which I have assumed—are open to doubt. It may be that the mechanism which I have imagined and described, convection of heat by means of a circulatory electric current, can account for only a part, perhaps a small part, of the total heat conduction of metals; but I trust that enough has been done to show that the possibilities of this mechanism are worthy of serious consideration.

I propose next to consider how far the ideas set forth in this paper will go toward explaining the various "transverse" electro-magnetic and hermomagnetic effects in metals.

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[1] These PROCEEDINGS for April, 1918, pp. 98–103. I there used in turn "hypothesis A" and "hypothesis B" concerning the behavior of the free electrons as a gas. In nearly all that follows I have used "hypothesis A" which is that, aside from electric influences, the free electrons tend to equality of gas pressure throughout the bar, whereas "hypothesis B" assumes that they tend to follow the law of "thermal effusion."

[2] These PROCEEDINGS for March, 1920, pp. 139–154.

[3] Strictly, $\lambda'_0$ was used here instead of $\lambda'_c$, with the same meaning.

[4] These PROCEEDINGS, **6,** 1920 (617).

[5] It seems probable that in dealing with the conditions at the junction of two metals we really need to use the conception of number-density of free electrons in the "co-volume" of each metal. In fact, $n$ may without harm be interpreted as having this meaning in all my formulas except the one, taken from Drude, in which I express the free-electron conductivity in terms of mean free path, mean velocity, etc., of the free electrons. See the latter part of this paper, where $\gamma$, the grade of ionization, is estimated.

[6] Estimated by use of the Wiedermann-Franz ratio (average for 12 metals) applied to $k_o$ and $k_{100}$.

[7] Mean value, according to Lorenz (1881) between 0° C. and 100° C.

[8] See note under Cobalt.

[9] $\theta_{18}$ is given as 0.35 on the authority of Coolidge.

[10] These PROCEEDINGS, **6,** 1920 (617).

[11] *Physical Review*, May, 1919.